EPA Region 10 SOP For the Validation of Polychlorinated Dibenzodioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data

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The Office of Quality Assurance (OQA) of EPA Region 10 has developed the following guidelines which should be used to access the quality of PCDD and PCDF data from samples originating from Region 10 sampling sites. This SOP is based upon the data validation principles specified in National Functional Guidelines For Organic Data Review, December, 1990, and the quality control (QC) requirements of EPA Method 1613B, October, 1994, and EPA Method 8290, Revision 0, 9/94.

The EPA Analytical Operations Branch (AOB) of the Hazardous Site Evaluation Division in EPA Headquarters recently prepared a draft SOP for the validation of dioxin/furan data using low resolution GC/MS and Contract Laboratory Program (CLP) protocol, DFLM01.1. The title of this AOB SOP is, National Functional Guidelines For Dioxin/Furan Data Validation, January, 1996. This draft SOP does not apply for the validation of high resolution GC/MS data from EPA Methods 1613B and 8290, because CLP protocol DFLM01.1 uses a different procedure to calibrate the GC/MS system, and because the quality control requirements of CLP protocol DFLM01.1 are very different from the QC approach in high resolution methods 1613B and 8290. Therefore, National Functional Guidelines For Dioxin/Furan Data Validation, January, 1996, will not be used as the basis for the validation of Method 1613B and Method 8290 high resolution GC/MS data in EPA Region 10.

The validator of PCDD and PCDF data should obtain a copy of the site-specific Quality Assurance Project Plan (QAPP) and use the Data Quality Objectives and QA requirements of the QAPP to assess the data. This SOP requires that the following criteria be evaluated when determining the quality of high resolution PCDD and PCDF data:

1.0 HOLDING TIME AND PRESERVATION OF SAMPLES

1.1 Objective. To determine the validity of the measurement results based upon EPA requirements for preservation and holding time of the samples from day of collection to day of extraction. EPA also has holding time requirements for extracts which is the time from extraction of the samples to injection of the sample extracts.

1.2 Criteria. Holding time and preservation requirements for the measurement of 2,3,7,8-TCDD in water samples under the CWA (40CFR Part 136), SDWA, and RCRA

have been promulgated and codified under 40CFR. These regulations require that water samples be preserved by neutralizing any chlorine residual with 0.008% sodium thiosulfate, and cooling to 4°C using a holding time of 7 days from day of collection to day of extraction of the sample. In addition, the maximum holding time of extracts is 40 days from day of extraction to day of injection of the extract.

The holding time and preservation requirements of 2,3,7,8-TCDD and of other measured PCDD and PCDF isomers in non-water matrixes have not been promulgated by EPA. Therefore, the data validator should use the holding time specified in the EPA approved site-specific Quality Assurance Project Plan (QAPP).

> Method 8290, Revision 9/94 specifies that all samples, except fish and adipose tissue samples, must be stored at 4°C in the dark, extracted within 30 days, and completely analyzed within 45 days of extraction. Fish and adipose samples must be stored at -20°C in the dark, extracted within 30 days, and completely analyzed within 45 days of collection (see Section 6.4 of Method 8290).
>
> Method 1613B does not set holding times for PCDD or PCDF isomers. The Method does state that water samples which contain a chlorine residual should be treated with 80-mg of sodium thiosulfate per liter of water, samples should be maintained at 4°C in the dark, and extracts should be analyzed within 40 days of extraction.
>
> Method 1613B, October, 1994, has recommended a holding time of one year for tissue samples which are frozen at < -10°C. Once frozen tissue samples are thawed, tissue samples must be extracted within 24 hours.

It should be noted that the above reference data validation SOP, National Functional Guidelines For Dioxin/Furan Data Validation, January, 1996, does not address either holding time or preservation requirements for environmental samples which are measured for PCDDs/PCDFs.

1.3 Action. If **40CFR Part 136** and the QAPP for the samples do not specify a holding time, then the holding time which is recommended by applicable EPA method -- Method 1613B or EPA Method 8290, Revision 9/94, should be used. Whenever samples or extracts are analyzed after holding time expiration date, the results should be considered to be minimum concentrations and must be qualified with a "J3". Samples which are not preserved correctly should be qualified with a "J" flag.

2.0 GC/MS PERFORMANCE CHECK

2.1 Objective. Gas chromatograph/mass spectrometer (GC/MS) instrument performance checks are performed to ensure mass resolution, identification, and to some degree, sensitivity. These criteria are not sample specific. Conformance is determined using standard materials, therefore, these criteria should be met in all circumstances.

2.2 Criteria. For the PFK molecular leak, the resolution must be greater than or equal to 10,000. The deviation between the exact mass and the theoretical mass (Table 3 in 1613B) for each of the three to five ions monitored must be less than 5 ppm. If the mass spectrometer is adjusted the resolution must be tested again and the resolution documented. (1613B/10.1.2.2; 8290/7.6.2.2)

The mass spectrometer shall be operated in a mass-drift correction mode using PFK to provide lock-masses. Each lock-mass shall be monitored and shall not vary by more than +/-20% throughout each respective time window. (1613B/10.2.1.2)

Ion abundance ratios. All labeled and unlabeled PCDDs and PCDFs in the CS1 standard shall be within the QC limits in 1613B Table 3A or 8290 Table 8 for their respective ion abundance ratios. (1613B/10.2.2; 8290/7.7.2.3)

The HRGC/HRMS must meet the minimum levels in 1613B Table 2. All labeled and unlabeled analytes in the CS1 calibration standard must have signal to noise ratios greater than or equal to 10.0. (1613B/10.2.3)

The absolute retention time of $^{13}C_{12}$-1,2,3,4-TCDD shall exceed 25.0 minutes on the DB-5 column, and the retention time of $^{13}C_{12}$-1,2,3,4-TCDD shall exceed 15.0 minutes on the DB-225 column. (1613B/10.2.4)

The compound pairs in the window defining mixtures shall be determined and meet the elution requirements of Table 5. (1613B/10.3)

The height of the valley between the most closely eluted isomers and the 2,3,7,8-substituted isomers shall be less than 25% (1613B/10.4.2)

2.3 Action. Failure to meet either the resolution or the retention window criteria invalidates all calibration or sample data collected during the 12 hour time window.

3.0 INITIAL CALIBRATION

3.1 Objective. Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative

and quantitative data for PCDDs and PCDFs. Initial calibration demonstrates that the instrument is capable of producing a linear calibration curve.

3.2 Criteria. There shall be an initial calibration curve consisting of five points for each analyte. The initial calibration curve shall be determined less than 30 days from the time the first samples of a Sample Delivery Group (SDG) are measured by the lab. The lab shall use the same calibration standards with the same lot number, for all internal standards, and labeled standards used in measuring the initial calibration curve, verification standards, field samples, and method blanks on both the primary GC column and on the secondary confirmation GC column. If an analyte is calculated by the isotope dilution method, an averaged response factor may be used if the RSD is less than 20% For analytes calculated by the internal standard method, an averaged response factor may be used if the RSD is less than 35%. Otherwise, for either calculation method, the complete curve must be used (1613B/10.5.4). [There is a variance with 8290 which requires 20% and 30% respectively and also requires the use of the average RF.]

3.3 Action. If the Initial Calibration Curve is older that 30 days, or if internal standards or labeled standards used in measuring of the initial calibration curve, verification standards, field samples, and method blanks on both the primary GC column and on the secondary confirmation GC column or not from the same lot number, then all measurement data should be qualified with a "J" qualifier and non-detects qualified "UJ".

If the RSD exceeds 20% for those analytes analyzed by isotope dilution or 35% for those analytes analyzed by the internal standard method qualify positive results with "J", and non-detects qualified "UJ". At the reviewer's discretion, a more in-depth review may be conducted to minimize data qualification by examining the entire curve and the quantitation method used.

4.0 CALIBRATION VERIFICATION MEASUREMENTS

4.1 Objective. Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument remains capable of producing acceptable qualitative and quantitative data.

4.2 Criteria. The individual analytes shall meet the acceptance criteria in Table 7 of 1613B. [Method 8290 requires that the RRFs of the unlabeled analytes to be within 20% and the labeled analytes to be within 30%.

It should be noted that CLP protocol DFLM01.1 require that the GC/MS system must be calibrated based upon a daily Calibration Check Standard, whereas, EPA Methods 1613B and 8290 required that the GC/MS system the criteria of a daily calibration verification standard must be met with each 12-hour batch of samples measured, and that responsed factors for native target compounds are derived from the 5-point initial calibration."

4.3 Action. The reviewer should use professional judgement to determine if it is necessary to qualify the data. The following are guidelines:

> If the %D for an analyte is outside the acceptance window qualify positive results "J" and non-detected "UJ" for that analyte. If the ion abundance criteria are not met results qualify all results for that analyte "R".

5.0 SYSTEM PERFORMANCE

5.1 Objective. The performance of the method by the laboratory is examined by determination of their initial ability to perform the method (Initial Precision and Recovery (IPR) study) and demonstration of continuing ability to perform the analysis (PAR). See Section 8.2 of Method 1613B for requirements of IPR data.

As part of measuring system performance, Methods 1613B and 8290 require that samples and standards be measured within require QC limits. QC criteria such as required relative retention times of labeled and native isomers, theoretical ion abundance ratios, recovery limits for OPR and VER standards, and recovery limits for spiked labeled target compounds must be met in order to demonstrate that the measurement system is within control limits.

5.2 Criteria. Initial precision and accuracy. All cleanup steps used in processing samples shall be included in the IPR study. All analytes shall be within the IPR limits in Table 7 of 1613B. Note that Method 8290 does not require a IPR study.

Ongoing Precision and recovery (PAR). There will be one PAR sample for each sample set analyzed. All analytes must meet the PAR limits in Table 7. [There are no requirements for PAR samples in Method 8290.]

QC limits such as required relative retention times of labeled and native isomers, theoretical ion abundance ratios, recovery limits for OPR and VER standards, and recovery limits for spiked labeled target compounds must be within control limits of the method.

5.3 Action. Results for analytes which do not meet either IPR or PAR requirements should be qualified with either "J" or "UJ".
If an analyte is not recovered for an PAR sample, results must be qualified with an "R" for that analyte. Failure to meet QC limits of the method may result in measurement values to be qualified with a "J" or "UJ". In specific cases where major QC limits are exceeded, the data validator may determine that the measurement system is out of control, which would require that measurement results be qualified with a "J", "UJ", or "R" flag.

6.0 METHOD BLANKS

6.1 Objective. To determine the existence and magnitude of contamination of samples resulting from laboratory activities. The criteria for evaluation of blanks will apply to any blank associated with the samples, including any method blanks, instrument blanks, field equipment blanks, transfer blanks, trip blanks, or solvent blanks.

6.2 Criteria.

1. The criteria for the frequency of extraction and analysis of method blanks as stated in section 8.5 of Method 1613B shall be followed and demonstrated in the documented data. The maximum amount of PCDD and PCDF isomer contamination in method blanks is stated in Table 2 of Method 1613B.

2. The method blank must be measured on each GC/MS system which is used to measure a group of samples. This requirement includes measuring method blanks on a second GC column if confirmatory analysis of sample extracts on a second column is required by the method or by the Lab SOW.

6.3 Action. If the maximum contamination requirements of specific TCDD and TCDF isomers stated in Table 2 of Method 1613B are not met, then all isomers in all samples associated with a method blanks shall be qualified with a "J1" flag. If the frequency of measuring method blanks is not met by the laboratory in the data submitted, then the results of all samples which do not meet the frequency of extraction and measurement of method blanks shall be qualified with a "R" flag. Any PCDD or PCDF measurement in a sample that is also measured in any associated blank, is qualified with a "U" flag if the sample concentration is less than 5 times the blank concentration.

7.0 RECOVERY OF C-13 LABELED ISOTOPE DILUTION INTERNAL STANDARDS

7.1 Objective. Labeled PCDDs and PCDFs are added to each sample and method blank prior to extraction. The role of these C-13 labeled spiked compounds is to be an internal standard for the quantitation of native PCDD and PCDF isomers, and to serve as surrogates for the assessment of method performance in the sample matrix.

7.2 Criteria. The recovery of each C-13 labeled PCDD and PCDF isomer using Method 1613B must be within 25-150%. The acceptable recovery limits for Method 8290 data must be between 40 and 135%.

7.3 Action. If any of the 15 labeled percent recoveries are outside the guideline windows for individual analytes, the individual isomer for that sample will be qualified with a "J" flag. For non-detected PCDD and PCDF compounds whose percent recoveries are outside the guideline windows for individual analytes, these will be qualified with a "UJ" flag.

8.0 INSTRUMENT RECOVERY INTERNAL STANDARDS

8.1 Objective. The purpose of adding the two instrument recovery internal standards ($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD) prior to injecting sample extracts and standards into the GC/MS is to determine the recovery efficiency of the extraction and cleanup procedures, to determine if the GC/MS sensitivity and response are stable during every analytical run, and to determine if the same amount of extract was injected into the GC/MS.

8.2 Criteria. The sum of the area counts of two masses for each of the two instrument recovery internal standards for samples, blanks, and standards must not vary by more than a factor of four (-25% to +400%) from the sum of the associated average areas from the five initial calibration standards.

8.3 Action. The reviewer should use professional judgement to determine if it is necessary to qualify the data. The following are guidelines:

1. If the sum of the two quantitation area counts of either of the two instrument recovery standards in the samples or blanks are outside the -25% to +400% window, then positive results for compounds measured should be qualified with a "J".

2. If the sum of the two quantitation area counts is greater that 400%, then non-detected compounds should not be qualified.

3. If the sum of the two area counts is less than 25%, then non-detect compounds should be qualified with a "UJ".

4. If the sum of the area counts is less than 10%, then non-detect target compounds should be qualified with a "R".

9.0 PROJECT AND REGIONAL QUALITY ASSURANCE SAMPLES

9.1 Objective: The data validator should consider the data of samples which are identified as field duplicates, transfer blanks, trip blanks, blind spikes, blind blanks, and performance evaluation (PE) samples.

9.2 Criteria. If QA samples are included among the field samples for measurement by the laboratory, then the data validator should refer to the applicable QAPP for any QA requirements regarding QA samples. Results from the measurement of project and regional QA samples will reflect upon the ability of the laboratory to report analytical results of known and documented quality which meet the PARCC requirements of the QAPP.

9.3 Action. The data validator should recommend action in accordance with Regional specifications and the criteria for acceptable PE sample results. Poor performance by the laboratory on blind PE samples may indicate that the laboratory analytical system is out of control, or that the amount of PCDD and PCDF isomers reported by the laboratory is an estimated quantity. The data validator should use her/his professional judgement to assess if "J" or "R" qualifiers should be placed upon the data due to the measurement of QA or PE samples.

10.0 COMPOUND IDENTIFICATION

10.1 Objective. The qualitative criteria for target compound identification have been established by EPA Method 1613B and EPA Method 8290 to minimize the number of erroneous identifications. An erroneous identification can be either a false-positive (reporting a target compound when it is not present in the sample), or false-negative (not reporting a compound that is present in the sample). The addition of single or double blind PE samples among field samples provides ancillary data to support the laboratory's ability to meet QAPP objectives.

10.2 Criteria. EPA Method 1613B and EPA Method 8290 specify certain requirements and guidelines for the positive identification of certain PCDD and PCDF isomers. The most frequently encountered interfering compounds to the measurement of PCDDs and

PCDFs are chlorinated substances such as polychlorinated diphenyl ethers (PCDPEs), polychlorinated biphenyls (PCBs), polychlorinated alkyldibenzofurans, and polychlorinated napthalenes that may be found at concentrations several orders of magnitude higher than the analytes of interest. Interferences are such a major problem to Methods 1613B and 8290, that each method requires that PCDPE interference ions be scanned at the same time that PCDD and PCDF mass ions are measured. Both methods require that certain PCDF isomers such as 2,3,7,8-TCDF be measured on a second dissimilar GC column before specific TCDF identifications can be made.

In this part of the SOP for the validation of PCDD and PCDF data, the following criteria must be met for a GC peak to be identified as a PCDD or PCDF (either unlabeled or labeled compound):

1. The signals for the two exact m/z's being monitored must be present, and must maximize within plus or minus 2 seconds of one another (see 1613B/Section 15.1; 8290/Section 7.8.4.1.4).

2. The signal-to-noise ratio (S/N) of each of the two exact m/z's must be greater than or equal to 2.5 for a sample extract, and greater than or equal to 10 for a calibration standard (see 1613B/Section 15.2; 8290/Section 7.8.4.3).

3. The ratio of the integrated ion currents (EICPs) of both the exact m/z's monitored must be within the limits of the method (see 1613B/Section 15.3; 8290/Section 7.8.4.2).

4. The relative retention time (RRT) of the peaks representing a unlabeled 2,3,7,8 substituted PCDD or PCDF must be within the limits given in the method. The retention time (RT) of peaks representing non-2,3,7,8-substituted PCDDs or PCDFs must be within the RT windows established in the method (see 1613B/Section 15.4; 8290/Section 7.8.4.1.1).

5. The measurement of 2,3,7,8-TCDF on the primary DB-5 GC column must be confirmed by analysis on a confirmatory column such as DB-225, SP-2330, DB-DIOXIN, or equivalent. All QC requirements of the method must be met on both the primary and secondary GC columns (see 1613B/Section 15.5; 8290/Section 3.4). If a PCDPE interference peak to the measurement of 2,3,7,8-TCDF is detected on the secondary GC column, then the laboratory should remove PCDPE interferences by additional cleanup procedures such as is described in one of the following references:

a) Method 1613B, October, 1994, Section 13.1.2 and Section 13.4

(Alumina column cleanup).

b) J. R. Ryan, R. Lizotte, and W. H. Newsome, J. of Chromatography, 303 (1984) 351-360 (Activated Florisil column cleanup.

6. If non-PCDPE interferences to the measurement of 2,3,7,8-TCDF on the secondary GC column are present, then the laboratory should measure 2,3,7,8-TCDF on a third dissimilar GC column in order to separate the 2,3,7,8-TCDF peak from the non-PCDPE interference peak. Measurement of 2,3,7,8-TCDF on a third dissimilar GC column requires full calibration (both initial and calibration verification) on the third GC column.

7. The identification of a GC peak (on either primary or confirmatory GC column) as a PCDF can only be made if no signal having a S/N $\geq$ 2.5 is detected at the same retention time (± 2 seconds) in the corresponding polychlorinated diphenyl ether (PCDPE) channel. This criteria requires that the laboratory document the EICP of all PCDPE m/z's which are scanned (see 8290/Section 7.8.4.4).

8. The retention times of target compounds must be verified using reference standards before identifications can be determined (see 8290/Section 3.3).

9. The valley height between 2,3,7,8-TCDD and the other TCDD isomers at m/z 319.8965, and between 2,3,7,8-TCDF and the other TCDF isomers at m/z

303.9016 shall not exceed 25% on their respective columns (see 1613B/Section 14.4.2.2; 8290/Section 7.9.7.1.1 and 7.9.7.1.2).

10.3 Action. The validator of the data must use his/her professional judgement in evaluating the data using the above identification criteria. Generally, if all of the above criteria for the identification of PCDD and PCDF isomers are not met, then each reported positive measurement of a PCDD or PCDF isomer should be considered a non-detect, and therefore flagged with a "R" flag. The "R" flag in this case is based upon the fact that the presence of the isomer in the sample can not be corroborated by the laboratory data.

11.0 LABORATORY CONTACTS

Provide and attached to the validation memo a copy of all telephone logs and correspondence with the laboratory concerning the quality of data submitted by the laboratory.

12.0 OVERALL ASSESSMENT OF THE QUALITY OF THE DATA

12.1 Objective. The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments of the quality of the data. The overall assessment of the data should be made after the data validator considers the DQOs and other QA requirements of the site-specific QAPP. It should be noted that the data reviewer does not determine or report the useability of the data. This determination is made by the Site Manager and by the other users of the data.

12.2 Criteria. The criteria for overall assessment is the QA and DQO criteria of the QAPP and the criteria listed above in this data validation SOP.

12.3 Action. Use professional judgement to determine if there is a need to further qualify the data. Write a brief narrative to give the user an indication of any analytical limitations of the data. Note if there are any inconsistencies observed between the raw data and the laboratory reported sample results.

DATA QUALIFIER DEFINITIONS

U - The analyte was analyzed for, but was not detected above the sample quantitation limit. The associated numerical value indicates the approximate concentration necessary to detect the analyte in this sample.

If a decision requires quantitation of the analyte below the associated numerical level, reanalysis or alternative analytical methods should be considered.

J - The analyte was analyzed for and was positively identified, but the associated numerical value may not be consistent with the amount actually present in the environmental sample.

A subscript may be appended to the "J" that indicates which of the following quality control criteria were not met:

J1 Blank Contamination: indicates possible high bias and/or false positives.

J2 Calibration range exceeded: indicates possible low bias.

J3 Holding times not met: indicates low bias for most analytes with the exception of common laboratory contaminants and chlorinated ethenes (i.e.: trichloroethene, 1,1-dichloroethene, vinyl chloride).

J4 Other QC parameter outside control limits: bias not readily determined.

J5 Other QC parameter outside control limits. The reported results appear to be biased high. The actual value of target compound in the sample may be lower than the value reported by the laboratory.

J6 Other QC parameter outside control limits. The reported results appear to be biased low. The actual value of target compound in the sample may be higher than the value reported by the laboratory.

J7 2,3,7,8-TCDF is reported from the value measured on the primary GC Column, DB-5. The reported value on the primary GC column may be biased high because other TCDF isomers may elute at this same retention time. The actual value of 2,3,7,8-TCDF in the sample may be

lower than the value reported by the laboratory due to possible co-elution of other TCDF isomers on the primary GC column.

J8 The measurement of 2,3,7,8-TCDF on the secondary GC column used by the Laboratory appears to have chemical interferences which co-elute with the native 2,3,7,8-TCDF GC peak. Therefore, the value of 2,3,7,8-TCDF on the secondary GC column is rejected and is qualified with a "R" flag. Consequently, the measured value of 2,3,7,8-TCDF on the primary GC column should be used as the measured value of 2,3,7,8-TCDF in the sample. The reported value of 2,3,7,8-TCDF on the primary GC column is qualified with a "J8", and may be biased high because other TCDF isomers may elute at this same retention time. The actual value of 2,3,7,8-TCDF on the primary GC column may be lower than the value reported by the laboratory due to possible co-elution of other TCDF isomers.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet critical quality control criteria. The presence or absence of the analyte cannot be verified.

Resampling and reanalysis are necessary to confirm or deny the presence of the analyte.

UJ - The analyte was analyzed for and was not detected above the reported quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in this sample.

If a decision requires quantitation of the analyte close to the associated numerical level, reanalysis or alternative analytical methods should be considered.